AD-A047 938 PENNSYLVANIA STATE UNIV UNIVERSITY PARK DEPT OF MATE--ETC F/G 11/2
ENVIRONMENTAL EFFECTS UPON THE TIME-DEPENDENT FRACTURE OF SILIC--ETC(U)
NOV 77 R E TRESSLER DAHC04-74-G-0142

UNCLASSIFIED ARO-11769.6-MS NL

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

ARO 11769.6-MS

# REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: 11769

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle): Environmental Effects Upon the Time-Dependent Fracture of Silicon Nitride and Silicon Carbide.

5. TYPE OF REPORT & PERIOD COVERED: Final, June 1, 1974 - August 31, 1977

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s): Richard E. Tressler

8. CONTRACT OR GRANT NUMBER(s): DAH CØ4-74-G-Ø142, 76 G 0233

9. PERFORMING ORGANIZATION NAME AND ADDRESS: The Pennsylvania State University, Materials Sciences Department, University Park, PA 16802

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS: U. S. Army Research Office, Post Office Box 12211, Research Triangle Park, NC 27709

12. REPORT DATE: November 1977

13. NUMBER OF PAGES: 9

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): Final rept. 1 Jun 74-31 Aug 77; 11p.

15. SECURITY CLASS. (of this report): Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE: NA

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

ARO 11769.6-MS

DDC RECEIVED DEC 20 1977 D

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

18. SUPPLEMENTARY NOTES

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Silicon Nitride, Silicon Carbide, Fracture, Time-Dependent Failure, Environmental Effects on Fracture, Delayed Failure, Corrosion, Stress-Corrosion.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Crack growth behavior in commercially available silicon carbide and silicon nitride materials has been studied as a function of temperature in gaseous environments ($H_2O$, $SO_2$, $O_2$) using the double torsion technique to generate $K_I$-V diagrams from room temperature to 850°C. In the case of the hot-pressed and reaction sintered silicon nitride materials the $K_I$-V curves were insensitive to the test temperature and environment. The hot-pressed silicon carbide exhibited accelerated crack growth at temperatures greater than 750° in these

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404 352

AD A047938

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20. oxidizing gaseous environments.

The effects of molten salt exposure on the critical flaw sizes and $K_{Ic}$'s of hot-pressed and reaction-sintered $Si_3N_4$ were examined. Both $Na_2SO_4$ - NaCl eutectic and NaCl molten salts at 1000°C altered the critical flaw sizes for failure by corrosion and reduced the $K_{Ic}$'s of the surface zone which was contaminated by cation and anion penetration along the grain boundaries.

# "Environmental Effects Upon the Time-Dependent Fracture of Silicon Nitride and Silicon Carbide"

Final Technical Report

Richard E. Tressler

November 7, 1977

U. S. Army Research Office

Grant Numbers
DAH CO4 74 G 0142
76 G 0233

The Pennsylvania State University



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## Introduction

The great advantages, in terms of economy and performance, to be gained by using high performance ceramics in applications such as the gas turbine engine have spurred development efforts in the non-oxide ceramic area and in hardware applications. However, relatively little effort has been devoted to examining in detail the factors which may limit lifetimes in the above applications in which long lifetimes have been traditionally demanded. The purpose of this research project was to use a fundamentally based fracture mechanics approach to examine the susceptibility of $Si_3N_4$ and SiC ceramics to stress-corrosion in water and various gaseous environments over a range of temperatures. Further, the fundamental mechanism(s) which contribute(s) to the observed slow crack growth were to be elucidated. In addition, an effort was initiated to investigate the mechanism(s) by which molten salt environments may limit strengths and lifetimes of these materials.

The approach to date has been to use the double torsion specimen to determine the stress intensity (at the crack tip) vs. propagating crack velocity relationship for these materials in $H_2O$ and gaseous environments containing small amounts of $O_2$, $H_2O$, $SO_2$. From these data one can predict lifetimes at various stresses if the initial flaw size is known.

The molten salt studies have concentrated on examining the effect of the concentration of oxidant species on the corrosive etching rates of $Si_3N_4$ and SiC in $Na_2SO_4$, NaCl and mixtures of these; and to examine the penetration of contaminant species into the test materials. These studies were extended to examine the effects of

molten salt exposure on strength and the parameters which determine strength at room temperature and at elevated temperatures.

Most of this work has been written in the form of manuscripts for publication in the open literature. For the specific details these reports should be consulted. In the following sections the results and accomplishments are summarized briefly and in general terms.

## Crack Propagation Studies at Low Temperatures

From experiments at low temperatures (27°C to 78°C) in water and dry environments it was found that there was no significant effect of water on the stress intensity factor vs. crack velocity (K,V) curves for reaction sintered $Si_3N_4$. Similar conclusions were drawn for the hot-pressed $Si_3N_4$ except that in dry environments sub-critical crack growth could not be observed since the specimens always failed during precracking suggesting a moisture effect on crack initiation. In the case of the hot-pressed SiC materials there was a reproducible tendency for environments with water present to shift the (K,V) curves to lower K values (compared to dry environments) and to decrease the slope. However, the observed slopes for crack growth in moist environments were still very high (N>100) indicating that the moisture effect is not a significant factor as it is in some oxides and glasses.[1]

## Crack Propagation Studies at Elevated Temperatures

The detailed results for the SiC materials are given reference (2) and summarized more generally in reference (3). The major finding in this study is that a previously unreported stress corrosion mechanism causes crack growth at K values substantially

lower than $K_{Ic}$ and is a <u>significant</u> consideration for lifetime considerations in hot-pressed SiC. The tentative proposal is that the subcritical crack growth results from oxidation of the SiC. Current work is directed at characterizing the phenomenon in more detail.

The results for the $Si_3N_4$ materials are summarized in the paper to be published in the proceeding of the NATO ASI on Nitrogen Ceramics[4] and in reference (3). The general conclusions are reviewed here. For the reaction-sintered $Si_3N_4$, the data obtained in the various environments from 200°C to 800°C fell within the ranges observed near room temperature. These results indicate that the testing atmospheres and temperatures had a neglibible effect on sub-critical growth in this material in the range of crack velocities studied ($10^{-5}$ m/sec - $10^{-1}$ m/sec). All of the hot-pressed $Si_3N_4$ ceramics exhibited unstable crack propagation and arrest in the various gaseous environments from 200°-800°C. This mode of fracture appears to be related to microstructural inhomogeneities in these hot-pressed materials which produce variations in the intrinsic toughness of the material. If the initiation and arrest stress intensity factors are analyzed assuming that an energy balance criterion applies to this phenomenon of unstable propagation and arrest (rather than assuming that $K_{Ia}$ is equal to $K_{Ic}$ which is not indicated by these and other experiments), with the double torsion specimen using fixed grip conditions, the following relationship is derived: $K_{Ic} = (K_{Ii}K_{Ia})^{1/2}$. Neither the testing environments used in this study nor variations in the displacement rate affected the values of $K_{Ii}$ or $K_{Ia}$. The average values for the various

materials and the ranges of values are indicated in the above papers. The commercially available material showed the narrowest ranges of values of these parameters and also the lowest calculated $K_{Ic}$. The experimental materials with $Y_2O_3$ as a densification aid, which contained easily observable large scale inhomogeneities, showed much more variability in these parameters, but also significantly larger $K_{Ic}$'s particularly for the experimental grade 2.

Molten Salt Corrosion

The results of these studies are reported in references (5) and (6). Briefly, the most significant finding was that the $Si_3N_4$ materials corroded much less rapidly than the SiC materials in the salts with high $O^{2-}$ activities ($Na_2SO_4$, and the eutectic mixture of $Na_2SO_4$ and NaCl). As pointed out in reference (3) the $Si_3N_4$ material probably oxidizes to $SiO_2$ before dissolving in the molten salt while the SiC may oxidize to SiO gas and dissolve much more rapidly into the salt. Also, the fact that the salt ions diffuse into the $Si_3N_4$ material rapidly at 1000°C suggested that modified mechanical properties could be expected in environments which contain either condensed or gaseous salt of these types.

In reference (6) the details of the molten salt exposure effects on the strength limiting parameters, at room temperature and 1200°C, are presented for reaction-sintered and hot-pressed $Si_3N_4$. The experiments have shown that for relatively short exposure times the critical flaw sizes are substantially increased and the $K_{Ic}$ values of the surface region are measurably reduced in the case of the hot pressed material. The more oxidizing eutectic mixture of NaCl-$Na_2SO_4$ caused greater flaw size increases and lesser

$K_{Ic}$ decreases than the less oxidizing NaCl melt. The results at 1200°C show evidence for subcritical crack growth which is similar to that observed for untreated, hot pressed $Si_3N_4$.

The apparent $K_{Ic}$ values for the sintered material are not much affected by the molten salt exposure except for the material exposed to the eutectic mixture in which the apparent $K_{Ic}$ at 1200°C was double that of the untreated material. The strengths of these materials were dramatically reduced by molten salt exposure apparently due to increased surface flaw sizes.

Qualitative analyses of the affected zones of the test specimens indicated that the contaminants diffuse along the grain boundaries thus modifying the grain boundary controlled properties.

These results indicate the potential for significant degradation of the mechanical properties of $Si_3N_4$ after exposure to sodium containing oxidizing and relatively non-oxidizing molten salts.

The initial results on hot pressed SiC indicate similar drastic strength reductions after exposure to the molten salts. In particular, the NaCl treated specimens experienced strength reductions of nearly two thirds at room temperature and 1200°C after immersion in NaCl at 1000°C for 100 hours. The accurate and independent determinations of $K_{Ic}$ have not been performed as yet to establish the relative roles of surface flaw and $K_{Ic}$ (in the surface layer) alterations in this degradation phenomenon.

In reference (7) a related study on the source of critical flaws, in SiC, as the grain size and surface machining grit size was changed, is described. Failure initiated predominantly via the propagation of extrinsic machining induced flaws for the range of

grain sizes and machining grit sizes studied. These results are consistent with the region of large grain size control delineated by Prochazka and Charles. The severity of machining-induced flaws, relative to the machining grit size, decreased with increasing machining grit size and decreasing SiC grain size.

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